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NBS/EPA CERTIFIED REFERENCE MATERIAL PERFORMANCE AUDIT PROGRAM: STATUS REPORT 1

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16. ABSTRACT

A traceability procedure has been established which allows specialty gas producers to prepare gaseous pollutant Certified Reference Materials (CRMs). The accuracy, stability and homogeneity of the CRMs approach those of NBS Standard Reference Materials (SRMs). Part of this procedure is an independent quality assurance audit of each CRM batch by an EPA-coordinated auditor. As of August 1984, 33 candidate batches had been audited. In general, the agreement between the producer's analytical results and the audit results has been within plus or minus 0.5 percent relative. Additional data suggest that CRMs are stable during their two-year certification periods.

The purchaser of a CRM is assured that its accuracy is high because of four features of the CRM program:

1. The general technical procedure for producing and analyzing CRMs has been specified by NBS;
2. CRMs are directly traceable to SRMs which are used as reference standards during the analysis of CRMs;
3. The producer's analytical results are verified by measurements which are performed by an independent auditor; and
4. Both the producer's and the auditor's analytical results must be reviewed and approved by NBS before the CRMs may be sold.

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CONTENTS

1. INTRODUCTION 1

2. PROCEDURES FOR THE PRODUCTION OF CRMs 3

THE CRM PRODUCER 3
THE PERFORMANCE AUDIT PROGRAM FOR CRMs 4
NBS'S REVIEW OF THE RESULTS 13

3. CRM STABILITY AND RECERTIFICATION 16

4. QUALITY ASSURANCE FOR THE CRM AUDIT PROGRAM 23

5. SUMMARY OF CRM AUDITS 27

6. CRM AVAILABILITY. 35

7. CONCLUSIONS 37

8. ACKNOWLEDGEMENTS. 37

REFERENCES 38

TABLES

Number		Page
1	Producer's Analytical Results for a Batch of 47.2 Parts Per Million Carbon Monoxide in Nitrogen CRMs.	5
2	Producer's Analytical Results for a Batch of 1000 Parts Per Million Nitric Oxide in Nitrogen Standards Which do not Satisfy CRM Requirements	6
3	Analytical Instrumentation for CRM Performance Audits	8
4	Auditor's Analytical Results for Two Samples From a Batch of 47.2 Parts Per Million Carbon Monoxide in Nitogen CRMs	12
5	Comparison of Producer's, Auditor's and NBS's Analytical Results for Two Sets of Carbon Monoxide in Nitrogen Audit Samples	15
6	Data From Long-Term Stability Study of CRMs	17
7	Recertification Data for a Batch of CRMs Containing 50 ppm Carbon Monoxide in Nitrogen	20
8	Recertification Data for a Batch of CRMs Containing 43 ppm Carbon Monoxide in Air	21
9	Comparison of Auditor Measured Values with National Bureau of Standards Certified Values for "Unknowns"	24
10	Chronological Summary of CRM Audits	28
11	Comparison of Producer's Measured Value With Audit Results for All Carbon Monoxide in Nitrogen CRMs	29
12	Comparison of Producer's Measured Value With Audit Results for All Carbon Monoxide in Air CRMs	31
13	Comparison of Producer's Measured Value With Audit Results for All Nitric Oxide in Nitrogen CRMs	32
14	List of CRMs Which Have Been Approved for Sale	36

FIGURES

Number		Page
1	Stylized Representation of A Portion of A Strip Chart Trace From A Performance Audit of Certified Reference Materials	9
2	Frequency Distribution for the Concentration Change Between the First and Second Analyses of Selected CRM Audit Samples	18
3	Frequency Distribution for the Agreement Between RTI Measurements and NBS Certified Values for "Unknowns"	25
4	Frequency Distribution for the Agreement Between Producer and Auditor Analytical Results for CRM Batches	33

SECTION 1
INTRODUCTION

The legal implications of many environmental measurements make it necessary that accurate and stable standards be used to calibrate the monitoring instrumentation. In the past, U.S. Environmental Protection Agency (EPA) regulations have required that gaseous pollutant calibration standards for ambient air quality measurements be traceable to National Bureau of Standards (NBS) Standard Reference Materials (SRMs) (1). Similarly, calibration standards for mobile source emission measurements are required to be traceable to either NBS SRMs or other gas standards which have been approved by the EPA Administrator (2). SRMs were developed to provide more accurate standards than were available from commercial sources at the time (3). Since their introduction, they have become accepted as benchmarks for air quality measurements. This acceptance created a demand for SRMs which occasionally exceeds NBS production capacity and at times NBS's inventory of SRMs has been exhausted.

In response to this demand for more high-accuracy standards, NBS and EPA established a traceability procedure by which specialty gas producers can prepare standards whose accuracy approaches that of SRMs (4, 5). These standards are called Certified Reference Materials (CRMs). The traceability procedures details the criteria and requirements by which a specialty gas producer can produce certain gaseous mixtures as CRMs and have them certified as being directly traceable to NBS gaseous SRMs. The purchaser of a CRM is assured that its accuracy is high because the general technical procedure for producing and analyzing CRMs has been specified by NBS; the analyses use SRMs as reference standards; the producer's analytical results are verified by an EPA-coordinated, independent performance audit; and all analytical results must be reviewed and approved by NBS before the CRMs can be sold.

Existing or proposed EPA regulations allow CRMs to be used as equivalents of SRMs for ambient air quality surveillance (6) and for

continuous emission monitoring systems (7). Similarly, CRMs have been approved for use in new motor vehicle certification (8) and in vehicle inspection and maintenance programs (9).

Since November 1980, the Research Triangle Institute (RTI) has been the EPA-coordinated, independent auditor for the CRM program (10). This work has been performed under various work assignments of EPA Contract Numbers 68-02-3431 and 68-02-3767. This report summarizes the CRM program in general and the audit program specifically.

As of August 1984, 31 batches of specialty gas producers' calibration standards have satisfied the requirements for CRMs. These CRMs contain carbon monoxide in nitrogen, carbon monoxide in air, or nitric oxide in nitrogen. Additionally, NBS and EPA have established procedures for the production of CRMs that contain sulfur dioxide in nitrogen, propane in nitrogen, or propane in air. A procedure for the production of carbon dioxide in nitrogen CRMs is under development. EPA maintains a list of all batches of CRMs that have been approved for sale (11).

SECTION 2
PROCEDURES FOR THE PRODUCTION OF CRMs

2.1 THE CRM PRODUCER

The NBS/EPA traceability procedure (5) specifies, in general terms, how specialty gas producers may prepare and analyze a batch of candidate CRMs. Although the specific details are left to the CRM producer to decide, enough has been spelled out in the procedure to assure that a producer can attain adequate accuracy. Some of the significant elements of the procedure are listed below:

- A SRM must be used as the reference standard for the analyses (although one cylinder from the CRM batch is used as an intermediate internal standard). It is important that the calibration chain between the SRM and the CRM be as short as possible to reduce the CRM's total uncertainty;
- When a CRM batch is produced, the batch mean concentration must lie within $\pm$ 1 percent relative of the concentration of the SRM to be used as the reference standard. As a result, error due to inadequate instrumental linearity will be reduced;
- Each CRM batch must contain at least 10 cylinders having identical concentrations. The batch must be large enough to allow valid statistical inferences to be drawn concerning the homogeneity of the batch and the concentration of individual cylinders in the batch;
- The CRM producer must demonstrate that the batch is homogeneous. Homogeneity can be demonstrated by comparing the distribution of the measured concentrations for the entire batch with the precision of the analytical method.
- The CRM producer must demonstrate that the batch is stable by performing two analyses of the batch that are separated by at least a month's time. If no appreciable concentration change has occurred, the batch is considered to be stable.

Table 1 gives an example of a CRM producer's analytical results for a batch of carbon monoxide in nitrogen CRMs. The reference SRM had a concentration of 47.1 ppm. It can be seen that the batch's overall mean concentration is very close to that value. The producer's results suggest that the batch is homogeneous because the standard deviation of the measured concentrations for the batch is similar to the standard deviation of the measured concentration for the internal standard (i.e., 0.137 ppm for the first analysis of the batch and 0.076 for the first analysis of the internal standard). The producer's results suggest that the batch is stable because the "paired difference" statistical test indicated that the differences between the first and second analyses were not statistically significant.

An example of a batch which did not meet the CRM requirements is given in Table 2 (12). The CRM producer analyzed a batch of nitric oxide in nitrogen CRMs on three separate occasions.

> "The data shows that several samples have decreased in concentration from one analysis to the next. This behavior suggests that some samples are unstable, but it would be difficult to prove that the lot is either stable or unstable" (Reference 12).

Because of these stability questions, this batch has not been certified as meeting the requirements for CRM's.

After a CRM producer is satisfied that a batch is homogeneous and stable, a letter containing the analytical results is sent to NBS for review. Additionally, the EPA-designated auditor is sent a letter which states that a CRM batch is available to be audited.

2.2 THE PERFORMANCE AUDIT PROGRAM FOR CRMs

The purpose of the EPA Performance Audit Program is to provide NBS with an independent set of analytical results for a CRM batch which NBS will use to verify the producer's analytical results. The audit is conducted on two samples from the batch which are selected at random by EPA. These samples are analyzed at an independent laboratory (in this case, RTI) which is funded by EPA. If the auditor's analytical results confirm the producer's analytical results, then NBS can conclude that

Table 1. Producer's Analytical Results For a Batch of 47.2 Parts Per Million Carbon Monoxide in Nitrogen CRMs.

Sample	First Analysis Concentration (ppm)	Second Analysis Concentration (ppm)	Difference (ppm)	Mean Concentration (ppm)
1[a]	47.197[b]	47.206[c]	+0.009	47.202
2	47.149	47.239	+0.090	47.194
3	46.941	47.167	+0.226	47.054
4	47.197	47.144	-0.053	47.170
5	47.178	47.201	+0.023	47.190
6	47.244	47.169	-0.075	47.206
7	47.263	47.167	-0.096	47.215
8	47.150	47.255	+0.105	47.202
9	46.847	47.350	+0.503	47.098
10	47.055	47.308	+0.253	47.182
11	47.282	47.192	-0.090	47.237
Mean	47.137	47.218	+0.081	47.177
Std. dev.	0.137	0.064	0.184	0.054

[a] Internal standard for the batch.

[b] The standard deviation for 11 measurements of the internal standard during the first analysis was 0.076 ppm.

[c] The standard deviation for 9 measurements of the internal standard during the second analysis was 0.114 ppm.

Table 2. Producer's Analytical Results for a Batch of 1000 Parts Per Million Nitric Oxide in Nitrogen Standards Which Did Not Satisfy CRM Requirements. (Source: Reference 12)

Sample No.	Concentration December 81 (ppm)	Concentration January 82 (ppm)	Concentration June 82 (ppm)	Difference June-Dec. (ppm)
1	954.1	953.3	951.6	-2.5
2	954.1	955.4	953.6	-0.5
3	953.8	954.0	953.5	-0.3
4	953.3	953.8	956.7	+3.4
5	955.0	954.7	950.8	-4.2
6	953.8	953.6	950.0	-3.8
7	953.7	953.1	952.4	-1.3
8	953.0	954.0	955.7	+2.7
9	954.4	953.5	952.2	-2.2
10	955.4	954.9	954.2	-1.2
11	953.9	955.4	954.7	+0.8
12	955.0	955.4	955.5	+0.5
13	955.6	954.6	954.7	-0.9
14	954.2	955.7	955.6	+1.4
15	954.5	955.4	954.7	+0.2
16	954.6	955.6	956.7	+2.1
17	954.3	953.5	961.5	-2.8
18	953.3	954.5	953.8	+0.5

Total Difference = -8.1

the producer has accurately measured the two samples and, by inference, the remainder of the batch. The general features of the audit have been specified in the NBS/EPA traceability procedure (5) with the details being left to the discretion of the auditor. Nevertheless, enough is spelled out in the traceability procedure to assure that the auditor can attain adequate accuracy. Some of the significant features of the audit procedure are listed below:

- The auditor randomly selects the two samples from the batch that will be audited. The producer is not aware which cylinders will be audited until after it has sent its analytical results to NBS.
- The auditor is not told the producer's analytical results until after the audit results have been sent to NBS. Thus, the auditor cannot subjectively interpret the audit data based on knowledge of the producer's analytical results.
- A SRM must be used by the auditor as the reference standard for the audit measurements. Thus, the auditor's and the producer's reference standards are tied to the same primary standards at NBS and the two sets of measurements may be validly compared.
- The auditor must make at least ten replicate measurements of each audit sample. This allows the precision of these measurements to be determined. The audit must be repeated if the standard deviation of the measurements exceeds 0.5 percent relative.

The detailed audit procedures and analytical methods used by RTI are adapted from those used by NBS in its analyses of SRMs (13). The analytical instrumentation used for the CRM audits are listed in Table 3. In general, the analytical procedure is identical for each of the measurement parameters. The contents of the audit samples, the reference SRM or the zero gas are fed without dilution through the analytical instrument by means of the cylinder's pressure alone. Each cylinder is connected through a pressure regulator and a solenoid valve into a common sampling manifold and needle valve. The pressure regulators are adjusted to yield the same flowrate through the instrument. The solenoid valves control which cylinder is being analyzed and are sequentially actuated by a digital timer. The measurement cycle is zero-SRM-CRM(1)-CRM(2) as is illustrated in Figure 1. This cycle is

Table 3. Analytical Instrumentation for CRM Performance Audits

Measurement Parameter	Analytical Instrumentation	Analytical Principle
Carbon Monoxide (0 to 1000 ppm)	Bendix 8501-5CA	Non-dispersive Infrared Spectroscopy
Carbon Monoxide (0.1 to 1 %)	Horiba PIR-2000	Non-dispersive Infrared Spectroscopy
Carbon Monoxide (1 to 10 %)	Perkin-Elmer 3920B	Gas Chromatography with a Thermal Conductivity Detector
Sulfur Dioxide	Thermo-Electron 40	Pulsed Ultraviolet Fluorescence Spectroscopy
Nitric Oxide	Thermo-Electron 10AR	Chemiluminescence Spectroscopy
Propane	Perkin-Elmer 3920B	Gas Chromatography with a Flame Ionization Detector

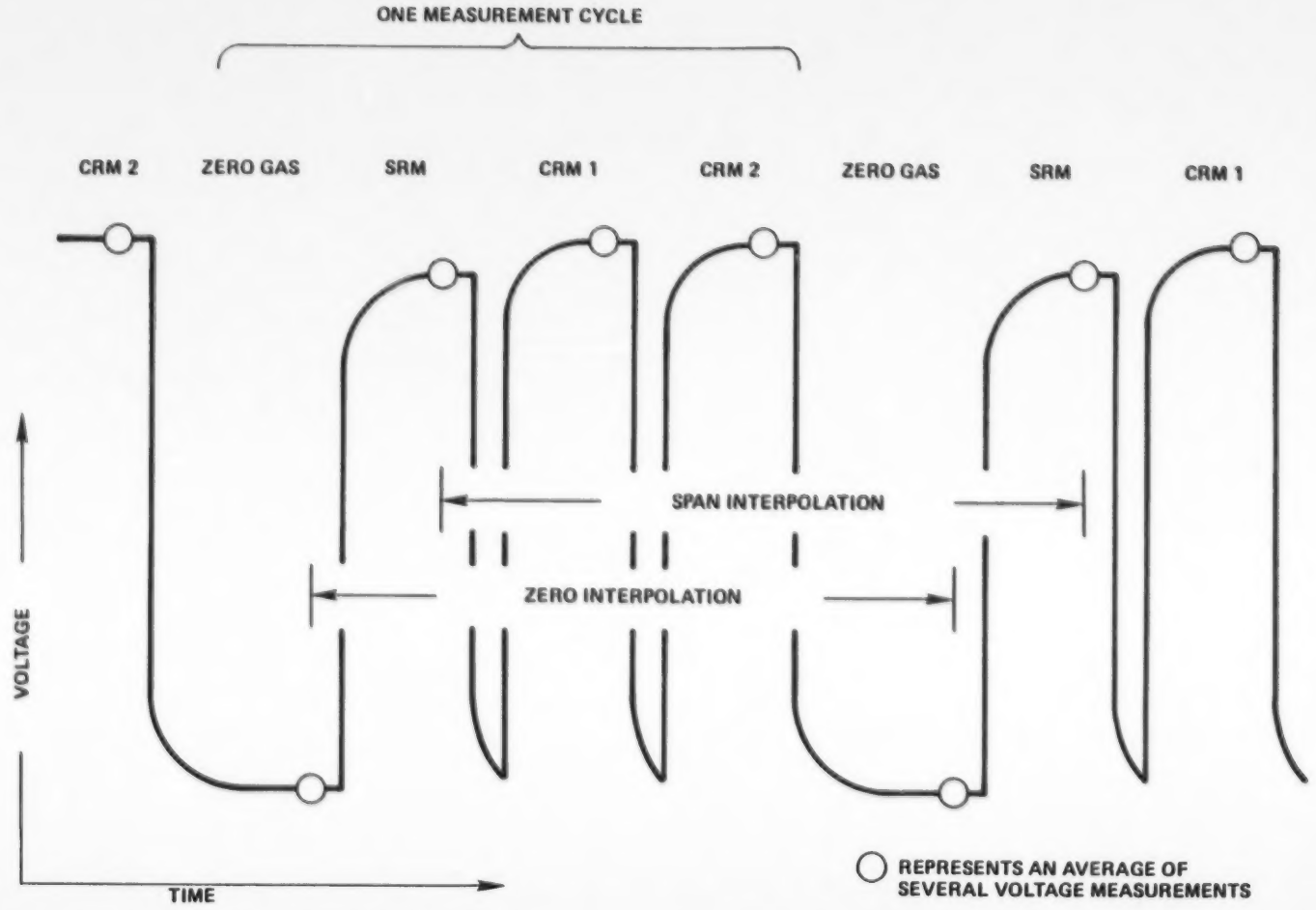

Figure 1. Stylized representation of a portion of a strip chart trace from a performance audit of Certified Reference Materials.

repeated at least ten times. Therefore, each set of CRM measurements is bracketed by a SRM measurement from its measurement cycle and one from the next measurement cycle. Each measurement in the cycle has a period from 5 to 15 minutes depending on the measurement parameter. Longer measurement periods are used for noisier signals. The voltage output from the instrument is recorded at regular intervals (e.g., 10 seconds) by a data logger. The data logger calculates a mean voltage for the last half or last third of each measurement period. The use of a data logger reduces the uncertainty due to short-term noise by producing a more precise value than could be obtained from an instantaneous voltage reading. A strip chart recorder is used to verify that the instrument's response is stable prior to the start of data collection. An instrument zero value and an instrument sensitivity are determined for each CRM measurement by interpolation between the two adjacent zero measurements and the two adjacent SRM measurements. This reduces the uncertainty due to long-term zero and span drifts. The sensitivities are multiplied by the zero-corrected mean CRM voltages to yield measured CRM concentrations.

One variation from this analytical procedure is used for nitric oxide CRM audits. Because the chemiluminescence instrument uses a high-vacuum reaction chamber, the gas cannot be pushed through the instrument. Instead, sample flows through the sampling manifold at atmospheric pressure at a rate slightly higher than the instrument requires. The instrument pulls what it needs from the sampling manifold and the excess is vented. It should also be noted that the oxides of nitrogen (i.e., nitric oxide and nitrogen dioxide) concentration is measured several times during an audit of nitric oxide CRMs. This allows calculation of the sample's nitrogen dioxide concentration which the NBS/EPA traceability procedure allows to be present at levels which may not exceed 1 percent of the nitric oxide concentration.

A second variation from the normal analytical procedure is used for high concentration carbon monoxide CRM audits. The gas chromatograph requires the use of a calculating integrator in the place of the data logger. The digital timer controls the sampling valve as well as the solenoid valves. At least ten injections are made during each measurement period.

the NBS/EPA traceability document requires that the instrumentation used in the audit be calibrated using several SRMs. One of these SRMs must be of the same nominal concentration as the CRM audit samples. The document also specifies that the auditor must be able to demonstrate the validity of the calibration of the instrument in the concentration range between the SRM and the CRM audit samples. RTI has chosen to calibrate the instrument using a single SRM and a zero gas over multiple measurement cycles as was discussed earlier. Such an approach is valid if the linearity of the instrument through this concentration range can be demonstrated. RTI has chosen to demonstrate such linearity through a linearity check. This linearity check is conducted either immediately before or immediately after the CRM measurements. The reference SRM, the zero gas and several other SRMs of differing concentration are measured in the same manner as the audit samples. The measurement cycle is zero-SRM(1)-SRM(2)-SRM(3)-etc. This measurement cycle is repeated at least three times. These data are averaged to yield a mean value for each SRM and the zero gas. Linear regression, quadratic regression or expoential regression are used to obtain a calibration curve from the mean values and the SRM concentrations. The deviation of each mean value from the calibration curve is used as an index of linearity. RTI has chosen a deviation of two percent relative to be its acceptance limit for linearity.

During and immediately after a CRM audit, measured data and ancillary information are transferred from the data logger/integrator output and the strip chart to a bound laboratory notebook. The physical records are then stored in the auditor's project files. The calculation of interpolated zero values, interpolated sensitivities and measured CRM concentrations are performed in the notebook. A mean and a standard deviation for the ten or more measured CRM concentrations are then calculated and recorded in the notebook. Finally, a statistical analysis of the linearity check data is performed and recorded in the notebook. All these calculations are performed by the auditor.

The auditor then prepares a written report of the audit. All mean voltages for the audit samples and the linearity check standards are included in the report. The procedures taken in calculating the mean

Table 4. Auditor's Analytical Results for Two Samples From a Batch of 47.2 Parts Per Million Carbon Monoxide in Nitrogen CRMs.

Analysis Number	Sample 5 Concentration (ppm)	Sample 7 Concentration (ppm)
1	47.275	47.278
2	47.281	47.281
3	47.271	47.266
4	47.266	47.294
5	47.289	47.310
6	47.270	47.289
7	47.275	47.288
8	47.293	47.310
9	47.276	47.278
10	47.269	47.267
Mean	47.276	47.286
Std. dev.	0.009	0.015

CRM concentration are explicitly shown. The report also includes information concerning the analytical instrumentation and the reference SRMs and presents the statistical analysis of the linearity check data. After this report has been prepared, it is sent to the RTI Quality Assurance Official for review and approval. The approved report is then sent to NBS and the EPA Project Officer.

Table 1 presented a producer's analytical results for a batch of carbon monoxide CRMs. The corresponding audit results for the same batch are given in Table 4. Sample 5 and 7 were chosen at random to be audited. For Sample 5, the mean audit value of 47.276 ppm is within 0.18 percent relative of the mean producer value of 47.190 ppm. For Sample 7, the mean audit value of 47.286 ppm is within 0.15 percent relative of the mean producer value of 47.215 ppm. Given the total uncertainty for both the producer's and the auditor's analytical results, a statistically significant difference does not exist between the two sets of results.

2.3 NBS'S REVIEW OF THE RESULTS

After NBS has received the producer's analytical results and the EPA-coordinated audit results, both sets of results are reviewed. The producer's analytical results must demonstrate that the batch is homogeneous and stable. The basic test to determine the homogeneity of the batch is a simple hypothesis test which compares the standard deviation of the measured concentrations of the entire batch with the standard deviation of replicate measurements of the internal standard. However, such a simple test does not address the possibility of individual outliers within the batch. Therefore, the producer's results are also examined as a distinct data set as well as graphically to ascertain the characteristics of the distribution of the measured concentrations and to identify possible outliers (if any) and their relationship of these and the measured concentrations of all other cylinders in the batch to the batch distribution to assess the homogeneity of the batch. The batch is judged to be stable if the distribution of differences between the first and second analyses for individual cylinders is random and is

not significantly different from zero. The concentration of the batch is judged to have been accurately measured if the audit results are not significantly different from the producer's analytical results.

In the event that NBS is not convinced that the batch is homogeneous, stable and accurately measured, NBS may request that the producer perform additional measurements of the batch or that the auditor perform additional measurements of the audit samples. Alternatively, NBS may have the auditor send the audit samples to NBS for an analysis. Such analyses have been necessary twice in the history of the program. The results of these analyses are given in Table 5. In these two cases, NBS's results confirmed the auditor's results.

If NBS is satisfied that a particular batch has satisfied the requirements for CRMs, it notifies EPA and the producer by letter. This letter gives measured concentrations for each member in the batch and will compare the producer's analytical results with the audit results. It also gives a total uncertainty associated with the measured concentrations.

In general, NBS remains the final arbiter concerning the homogenuity, stability and accuracy of each CRM batch. The active participation of NBS in the production of CRMs ensures their credibility as substitutes for SRMs.

Table 5. Comparison of Producer's, Auditor's and NBS's Analytical Results for Two Sets of Carbon Monoxide in Nitrogen Audit Samples

Producer's Results (ppm)	Auditor's Results (ppm)	Agreement[a] (Percent Relative)	NBS's Results (ppm)	Agreement[b] (Percent Relative)
9.91	9.94	+ 0.30	9.94	0.00
9.89	9.95	+ 0.61	9.94	+0.10
4698	4716	+ 0.38	4714	+0.04
4702	4708	+ 0.13	4710	-0.04

[a] $\text{Agreement} = 100 \left[\frac{\text{Auditor's Results} - \text{Producer's Results}}{\text{Producer's Result}} \right]$

[b] $\text{Agreement} = 100 \left[\frac{\text{Auditor's Result} - \text{NBS's Results}}{\text{NBS's Results}} \right]$

SECTION 3
CRM STABILITY AND RECERTIFICATION

During the development of SRM's, NBS found that the concentrations of carbon monoxide, nitric oxide, sulfur dioxide and propane mixtures contained in aluminum cylinders were stable for periods of two or more years. Accordingly, the original NBS traceability procedure for CRMs specified that a CRM batch may be certified for a period of two years following the batch's second analysis. If no significant concentration changes were found between the first and second analyses, then it was highly probable that the batch would remain stable during the two-year certification period. However, a batch could not be given an unlimited certification period. Concentration changes which would not affect the certified concentration over a two-year period may become significant after more than two years.

As CRMs were beginning to be produced, NBS and EPA decided to verify that the CRM's concentrations would remain stable through their two-year certification period. As a result, an informal long-term stability study was conducted with the cooperation of the CRM producers. NBS and EPA identified several previously-approved CRM batches as being of particular interest. The producers were contacted with the request that one of the two audit samples from each batch be returned to the auditor for reanalysis. During the winter of 1983, nine audit samples were reanalyzed. The period of time between the original audit and the long-term stability study reanalysis ranged from 11 to 25 months. The results of these measurements are listed in Table 6, and are presented as a histogram in Figure 2. In general, these data indicate the concentration changes are statistically significant. However, two points should be considered. First, the magnitudes of the concentration changes are small. Second, the statistical analysis does not include the relative uncertainty of the reference SRMs' concentrations in those cases where different SRMs were used for the two analyses. The largest variation observed was 0.29 percent relative after 25 months which is well within the total uncertainty of 1 percent relative for the sample's certified concentration. One cannot make broad statements

Table 6. Data From Long-Term Stability Study of CRMs

CRM Composition	Nominal CRM Concentration	Auditor Analysis Date	Mean Measured Concentration	Standard Error of Mean	Concentration Change[a] (Percent Relative)	Uncertainty[d] of Change (Percent Relative)
Carbon monoxide in nitrogen	50 ppm	January 1982 February 1983	47.29 ppm 47.34 ppm	<0.01 ppm 0.01 ppm	+ 0.11	± 0.05
	50 ppm	January 1981 February 1983	48.49 ppm 48.63 ppm	<0.01 ppm 0.02 ppm	+ 0.29	± 0.08
	50 ppm	January 1981 February 1983	47.19 ppm 47.31 ppm	<0.01 ppm 0.02 ppm	+ 0.25	± 0.08
	250 ppm	August 1981 March 1983	243.92 ppm 244.25 ppm	0.23 ppm 0.01 ppm	+ 0.14	± 0.17
	250 ppm	January 1982 March 1983	244.21 ppm 244.18 ppm	0.01 ppm 0.02 ppm	- 0.01	± 0.02
	1000 ppm	January 1982 March 1983	971.8 ppm 971.3 ppm	0.1 ppm 0.1 ppm	- 0.05	± 0.03
	1000 ppm	January 1982 March 1983	944.6 ppm 947.2 ppm	0.2 ppm 0.1 ppm	+ 0.28	± 0.04
Carbon monoxide in air	43 ppm	January 1982 February 1983	42.70 ppm 42.77 ppm	<0.01 ppm 0.01 ppm	+ 0.16	± 0.04
Nitric oxide in nitrogen	500 ppm	March 1982 February 1983	470.2 ppm 469.4 ppm	0.1 ppm 0.1 ppm	- 0.17	± 0.07

[a] $\text{Change} = 100 \left[\frac{\text{Second mean concentration - First mean concentration}}{\text{First mean concentration}} \right]$

[b] $\text{Uncertainty} = \frac{100\, t(0.975,\, n_1 + n_2 - 2)}{\text{First Mean Concentration}} \left[Se^2 \left(\frac{1}{n_1} + \frac{1}{n_2} \right) \right]^{1/2}$ where Se^2 is the pooled variance.

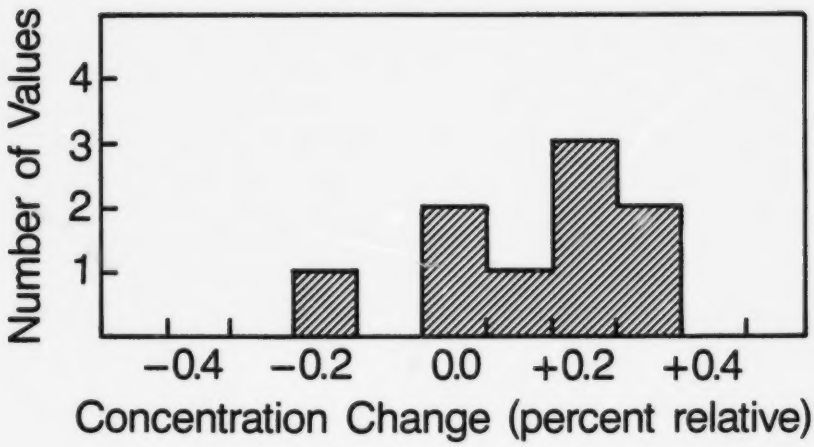

Figure 2. Frequency distribution for the concentration change between the first and second analyses of selected CRM audit samples.

concerning the long-term stability of all CRMs based on measurements of a few samples; nevertheless, these data are encouraging and suggest that CRMs will remain stable during their certification periods.

During the past year, NBS and EPA have developed an appendix (Appendix G) to the traceability document which allows CRM producers to recertify CRMs after their original two-year certification period has expired. The producers may take one of two approaches in the recertification. The first approach is to extend the certification of all unsold CRMs in a batch for a specified period following reanalysis of these samples (i.e., batch recertification). The second approach is to certify individual CRMs in a batch for a specified period beginning at the time of sale of each CRM to a purchaser (i.e., "date-of-sale" certification). In both cases, a reanalysis must be performed and the analytical results must be submitted to NBS for review and approval.

For batch recertification, all unsold CRMs are reanalyzed in a manner identical to the second analysis of the original certification. If the reanalysis demonstrates that the CRMs' concentration has not changed from that of the original certification, then the certification period may be extended for up to two years after the reanalysis date. As of this time, two batches of CRMs have been recertified using this approach. The first batch contains 50 ppm carbon monoxide in nitrogen. It was originally certified in May 1981 and was recertified in July 1983. During these 26 months, none of the 12 CRMs exhibited a significant concentration change. The original and reanalyzed concentrations for this batch are given in Table 7. The second batch contains 43 ppm carbon monoxide in air. It was originally certified in February 1982 and was recertified in July 1984. During these 28 months, 9 of the 10 CRMs did not exhibit a significant concentration change and were recertified. The remaining CRM showed signs of instability and could not be recertified. The original and reanalyzed concentrations for this batch are given in Table 8. These data suggest that, in general, CRMs remain stable through their certification period and may be recertified with confidence.

Table 7. Recertification Data for a Batch of CRMs Containing 50 ppm Carbon Monoxide in Nitrogen

Original[a] Concentration (ppm)	Reanalyzed[b] Concentration (ppm)	Change[c] (Percent Relative)
47.18	47.16	-0.04
47.18	47.17	-0.02
47.17	47.25	+0.17
47.20	47.17	-0.06
47.16	47.13	-0.06
47.21	47.12	-0.19
47.17	47.11	-0.13
47.17	47.22	+0.11
47.18	47.18	0.00
47.16	47.12	-0.08
47.19	47.22	+0.06
47.17	47.15	-0.04
	Mean	-0.02

[a] Batch originally certified in May 1981.

[b] Batch recertified in July 1983.

[c] $\text{Change} = 100 \left[\frac{\text{Reanalyzed Concentration} - \text{Original Concentration}}{\text{Original Concentration}} \right]$

Table 8. Recertification Data for a Batch of CRMs Containing 43 ppm Carbon Monoxide in Air

Original[a] Concentration (ppm)	Reanalyzed[b] Concentration (ppm)	Change[c] (Percent Relative)
42.3	42.3	0.00
42.4	42.3	-0.24
42.4	42.3	-0.24
42.3	42.4	+0.24
42.3	42.3	0.00
42.3	42.3	0.00
42.3	42.4	+0.24
42.3	42.3	0.00
42.3	42.3	0.00
42.4	42.2[d]	-0.47
	Mean	-0.05

[a] Batch originally certified in February 1982.

[b] Batch recertified in July 1984.

[c] $$\text{Change} = 100\left[\frac{\text{Reanalyzed Concentration} - \text{Original Concentration}}{\text{Original Concentration}}\right]$$

[d] This sample showed signs of instability and could not be recertified.

For date-of-sale certification, all CRMs in a batch are analyzed on three separate occasions over a six-month period prior to their original certification. At 18 months and 30 months after the batch's preparation, 20 percent (or at least 4) of the batch must be reanalyzed in a manner identical to the original analyses. The reanalysis results must be submitted to NBS for review. If none of the results suggest that a significant concentration change has occurred, an individual CRM may be certified for up to two years following its sale. As of this time, no CRM batches have been prepared and analyzed for date-of-sale certification.

SECTION 4
QUALITY ASSURANCE FOR THE CRM AUDIT PROGRAM

Quality assurance procedures for the CRM Audit Program are documented in its Quality Assurance Project Plan (14). This document received EPA approval in August 1984 and presents a detailed description of the quality assurance aspects of the program. Analytical and calibration procedures are described as well as are quality assurance objectives for precision, accuracy, completeness, representativeness and comparability.

The most important quality assurance objective for the program is accuracy. The use of SRM's as reference standards during the audits is the primary means to ensure accuracy. Additionally, there are two means to obtain an external evaluation of the accuracy of the audit program. The first means is the definitive analyses which NBS performs when there is a significant disagreement between the producer's analytical results and the audit results. As was shown in Section 3, NBS's results confirmed the audit results for two CRM batches.

The second means to evaluate the accuracy of the audit program is the analysis of "unknowns" by the auditor. Before the CRM producers begin to produce a particular class of CRMs, NBS evaluates the auditor's analytical ability to perform audits of this class by sending unknowns for analysis. These unknowns are well-characterized SRMs from NBS's inventory whose certified concentrations are unknown to the auditor. They are analyzed in the same manner as audit samples. There must be reasonably close agreement between the auditor's analytical results and the NBS-certified concentrations. As of this time, analyses have been conducted for 18 unknowns containing carbon monoxide in nitrogen, nitric oxide in nitrogen or sulfur dioxide in nitrogen. The results of these analyses are summarized in Table 9. Acceptable agreement was found for all 18 unknowns. The closest agreement was 0.00 percent relative and the poorest agreement was -0.56 percent relative. The mean of the absolute values of the agreement was 0.18 percent relative. A frequency distribution of the absolute values of the agreements is given in Figure 3. This level of agreement demonstrates

Table 9. Comparison of Auditor Measured Values with National Bureau of Standards certified values for "unknowns".

"Unknown" SRM Composition	Nominal SRM Concentration (ppm)	NBS Certified Value (ppm)	Auditor Measured Value (ppm)	Agreement[a] (Percent Relative)
Carbon monoxide in nitrogen	50	44.9	44.77	- 0.29
	50	45.3	45.29	- 0.02
	100	93.6	93.88	+ 0.30
	250	243.7	243.66	- 0.02
	500	476.	475.85	- 0.03
	1000	956.	953.16	- 0.30
Nitric oxide in nitrogen	50	47.8	47.82	+ 0.04
	100	96.4	96.53	+ 0.13
	250	235.4	235.23	- 0.07
	500	462.0	461.61	- 0.08
	1000	957.	957.27	+ 0.03
Sulfur dioxide in nitrogen	50	44.95	44.70	- 0.56
	100	95.1	95.10	0.00
	500	464.5[b]	463.1	- 0.30
	1000	940.	939.3	- 0.07
	1425	1428.	1431.	+ 0.22
	2375	2316.	2322.	+ 0.26
	3500	3122.	3138.	+ 0.52

[a] $\text{Agreement} = 100 \left[\frac{\text{RTI measured value - NBS certified value}}{\text{NBS certified value}} \right]$.

[b] Mean of original certified value of 459 ppm and a value of 470 ppm measured at NBS after the auditor's analysis. This SRM's concentration shifted as the cylinder pressure decreased.

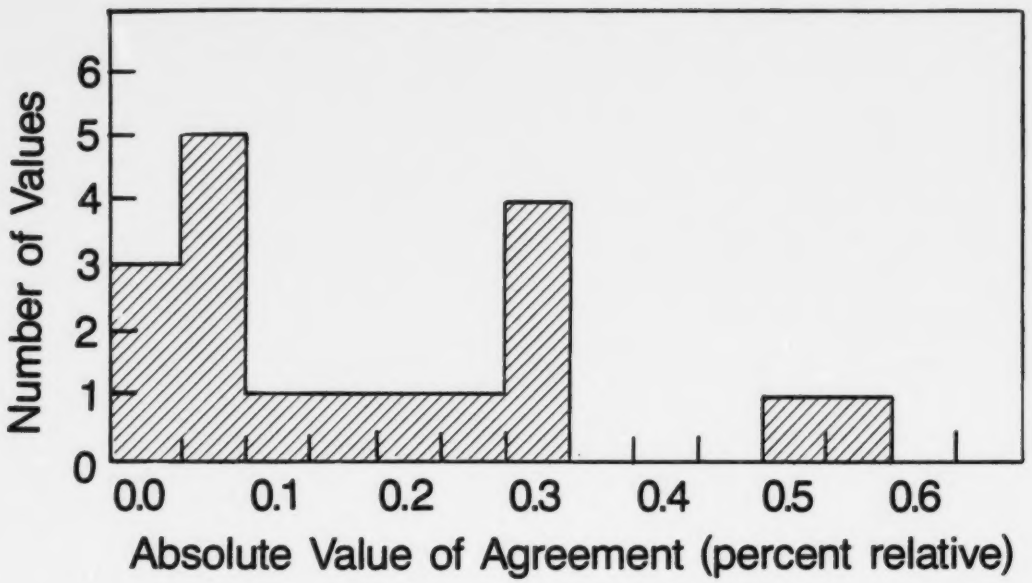

Figure 3. Frequency distribution for the agreement between RTI measurements and NBS certified values for "unknowns".

the ability of the auditor to measure gaseous calibration standards with a high degree of accuracy. Prior to any audits, this knowledge allowed EPA and NBS to implement the audit program with some degree of confidence.

SECTION 5
SUMMARY OF CRM AUDITS

As of August 1984, audits have been performed on 33 candidate CRM batches containing carbon monoxide in nitrogen, carbon monoxide in air or nitric oxide in nitrogen. A chronological summary of these audits is given in Table 10. For all 33 batches, acceptable agreement was obtained between the producer's measured values and the audit results. Two of these batches could not be certified because of problems not associated with the audit (i.e., batch instability and producer's analytical precision problems). The producer's measured values for all carbon monoxide in nitrogen CRM batches are compared with the audit results in Table 11. Similar comparisons are made in Table 12 for carbon monoxide in air CRM batches and in Table 13 for nitric oxide in nitrogen CRM batches. The frequency distribution of the absolute value of the agreement between the producer's and the auditor's measured values is given in Figure 4.

In general, the absolute value of the agreement has been within 0.5 percent relative. The mean absolute value of the agreement for the 66 audit samples is 0.19 percent relative. The maximum absolute value of the agreement is 0.61 percent relative. This level of agreement is within the limits set for the program and demonstrates that speciality gas producers can prepare and analyze CRMs with a high degree of accuracy.

The data in Tables 11 through 13 can also be used to give some indication of the precision of the audits. The coefficient of variation (COV) will be used as an index of precision. Non-dispersive infrared analyzers were used for carbon monoxide CRM audits at concentrations of 1 percent or less. The 44 audit samples in this concentration range had a mean COV of 0.05 percent and a maximum COV of 0.14 percent. A gas chromatograph with a thermal conductivity detector was used for carbon monoxide CRM audits at concentrations of 2 percent or greater. The 8 audit samples in this concentration range had a mean COV of 0.37 percent and a maximum COV of 0.56 percent. A chemiluminescence analyzer was used for nitric oxide CRM audits. The 10 nitric oxide audit

Table 10. Chronological Summary of CRM Audits.

Audit Date	CRM Producer	Certified Reference Material	Batch Status
Jan 81	Scott	50 ppm Carbon Monoxide in Nitrogen	Recertified
Jan 81	Airco	50 ppm Carbon Monoxide in Nitrogen	Certified
May 81	Airco	500 ppm Carbon Monoxide in Nitrogen	Certified
May 81	Airco	100 ppm Carbon Monoxide in Nitrogen	Certified
June 81	Airco	25 ppm Carbon Monoxide in Nitrogen	Certified
Aug 81	Airco	250 ppm Carbon Monoxide in Nitrogen	Certified
Dec 81	Airco	43 ppm Carbon Monoxide in Air	Recertified
Jan 82	Scott	250 ppm Carbon Monoxide in Nitrogen	Certified
Jan 82	Matheson	50 ppm Carbon Monoxide in Nitrogen	Certified
Jan 82	Scott	43 ppm Carbon Monoxide in Air	Certified
Jan 82	Airco	1000 ppm Carbon Monoxide in Nitrogen	Certified
Jan 82	Scott	1000 ppm Carbon Monoxide in Nitrogen	Certified
Feb 82	Airco	2500 ppm Carbon Monoxide in Nitrogen	Certified
Feb 82	Airco	8 % Carbon Monoxide in Nitrogen	Certified
Mar 82	Airco	500 ppm Nitric Oxide in Nitrogen	Certified
Mar 82	Airco	1000 ppm Nitric Oxide in Nitrogen	Uncertain[a]
Mar 82	Scott	10 ppm Carbon Monoxide in Nitrogen	Certified
Apr 82	Scott	25 ppm Carbon Monoxide in Nitrogen	Certified
Apr 82	Airco	5000 ppm Carbon Monoxide in Nitrogen	Certified
May 82	Airco	100 ppm Nitric Oxide in Nitrogen	Certified
May 82	Airco	10 ppm Carbon Monoxide in Nitrogen	Pending[b]
July 82	Scott	2500 ppm Carbon Monoxide in Nitrogen	Certified
July 82	Scott	5000 ppm Carbon Monoxide in Nitrogen	Certified
Aug 82	Airco	250 ppm Nitric Oxide in Nitrogen	Certified
Feb 83	Air Prod.	500 ppm Carbon Monoxide in Nitrogen	Certified
Feb 83	Scott	250 ppm Nitric Oxide in Nitrogen	Certified
Apr 83	Matheson	10 ppm Carbon Monoxide in Nitrogen	Certified
May 83	Air Prod.	50 ppm Carbon Monoxide in Nitrogen	Certified
Oct 83	Airco	4 % Carbon Monoxide in Nitrogen	Certified
Oct 83	Air Prod.	1 % Carbon Monoxide in Nitrogen	Certified
Oct 83	Air Prod.	5000 ppm Carbon Monoxide in Nitrogen	Certified
Jan 84	Air Prod.	2 % Carbon Monoxide in Nitrogen	Certified
Jan 84	Air Prod.	8 % Carbon Monoxide in Nitrogen	Certified

[a] Acceptable agreement was obtained between the producer's analytical results and the audit results. However, the batch could not be certified because the producer's results suggested some cylinders were unstable. The producer may have blown down this batch.

[b] Acceptable agreement was obtained between the producer's analytical results and the audit results. However, the batch could not be certified because the producer's results exhibited poor precision. In the near future, the producer will perform additional analyses of the batch to allow the batch to be certified.

Table 11. Comparison of Producer's Measured Value with Audit Results for All Carbon Monoxide in Nitrogen CRM Batches

Nominal CRM Concentration	Producer's Measured Value[a]	Audit Results # of Values	Audit Results Mean Measured Value	Audit Results Standard Deviation	Agreement (Percent Relative)[b]
10 ppm	9.91 ppm	11	9.941 ppm	0.005 ppm	+0.31[c]
	9.89 ppm	11	9.950 ppm	0.014 ppm	+0.61[c]
	9.542 ppm[d]	13	9.535 ppm	0.007 ppm	-0.07
	9.535 ppm[d]	13	9.540 ppm	0.009 ppm	+0.05
	9.806 ppm	15	9.800 ppm	0.010 ppm	-0.06
	9.806 ppm	15	9.800 ppm	0.006 ppm	-0.06
25 ppm	24.28 ppm	10	24.21 ppm	0.01 ppm	-0.29
	24.29 ppm	10	24.23 ppm	0.02 ppm	-0.25
	24.32 ppm	10	24.27 ppm	0.01 ppm	-0.21
	24.32 ppm	10	24.26 ppm	0.01 ppm	-0.25
50 ppm	48.39 ppm	10	48.49 ppm	0.01 ppm	+0.21
	48.42 ppm	10	48.50 ppm	0.01 ppm	+0.17
	47.16 ppm	10	47.19 ppm	0.01 ppm	+0.06
	47.20 ppm	10	47.19 ppm	0.01 ppm	-0.02
	47.19 ppm	10	47.28 ppm	0.01 ppm	+0.19
	47.22 ppm	10	47.29 ppm	0.02 ppm	+0.15
	47.12 ppm	11	47.19 ppm	0.01 ppm	+0.15
	47.16 ppm	11	47.20 ppm	0.01 ppm	+0.08
100 ppm	97.12 ppm	10	96.85 ppm	0.02 ppm	-0.28
	97.22 ppm	10	96.88 ppm	0.02 ppm	-0.35
250 ppm	243.9 ppm	10	243.9 ppm	0.5 ppm	0.00
	244.0 ppm	10	243.9 ppm	0.6 ppm	-0.04
	244.1 ppm	10	244.2 ppm	0.0 ppm	+0.04
	244.0 ppm	10	244.2 ppm	0.1 ppm	+0.08
500 ppm	472.5 ppm	10	473.0 ppm	0.1 ppm	+0.11
	472.9 ppm	10	472.9 ppm	0.1 ppm	0.00
	476.2 ppm	12	474.8 ppm	0.1 ppm	-0.29
	476.1 ppm	12	474.8 ppm	0.1 ppm	-0.27
1000 ppm	946.4 ppm	11	944.6 ppm	0.5 ppm	-0.19
	946.4 ppm	11	944.2 ppm	0.5 ppm	-0.23
	969.8 ppm	11	971.8 ppm	0.5 ppm	+0.21
	970.0 ppm	11	971.0 ppm	0.6 ppm	+0.10
2500 ppm	2404 ppm	10	2414 ppm	1. ppm	+0.42
	2406 ppm	10	2413 ppm	1. ppm	+0.29
	2406 ppm	12	2414 ppm	1. ppm	+0.33
	2404 ppm	13	2413 ppm	1. ppm	+0.37

Table 11. (continued)

Nominal CRM Concentration	Producer's Measured Value[a]	Audit Results # of Values	Audit Results Mean Measured Value	Audit Results Standard Deviation	Agreement (Percent Relative)[b]
5000 ppm	4683 ppm	11	4690 ppm	2. ppm	+0.15
	4682 ppm	11	4692 ppm	1. ppm	+0.21
	4698 ppm[e]	12	4716 ppm	2. ppm	+0.38[f]
	4702 ppm[e]	12	4708 ppm	1. ppm	+0.13[f]
	4650 ppm	12	4642 ppm	1. ppm	-0.17
	4650 ppm	12	4645 ppm	1. ppm	-0.11
1%	0.955 %	18	0.957 %	0.000 %	+0.21
	0.955 %	18	0.957 %	0.000 %	+0.21
2%	1.963 %	9	1.966 %	0.011 %	+0.15
	1.966 %	9	1.968 %	0.011 %	+0.10
4%	3.892 %	10	3.911 %	0.017 %	+0.49
	3.890 %	12	3.890 %	0.017 %	0.00
8%	7.71 %	10	7.721 %	0.012 %	+0.1
	7.71 %	9	7.727 %	0.017 %	+0.2
	7.717 %	11	7.696 %	0.022 %	-0.27
	7.700 %	11	7.695 %	0.024 %	-0.06

[a] Based on NBS's letter notifying EPA that the batch has met CRM specifications.

[b] $\text{Agreement} = 100 \left[\frac{\text{Audit Value} - \text{Producer's Value}}{\text{Producer's Value}} \right]$

[c] Definitive analysis by NBS indicated that the carbon monoxide concentration in these two samples are 9.94 ppm.

[d] This batch has not been certified due to poor precision for the producer's analytical results.

[e] This value is the producer's original analytical results. After the audit, it was revised.

[f] Definitive analysis by NBS indicated that the carbon monoxide concentrations in these two samples are 4714 and 4710 ppm, respectively.

Table 12. Comparison of Producer's Measured Value with Audit Results for All Carbon Monoxide in Air CRM Batches

Nominal CRM Concentration	Producer's Measured Value[a]	Audit Results			Agreement (Percent Relative)[b]
		# of Values	Mean Measured Value	Standard Deviation	
43 ppm	42.36 ppm	11	42.40 ppm	0.01 ppm	+0.09
	42.30 ppm	10	42.45 ppm	0.02 ppm	-0.35
	42.70 ppm	10	42.70 ppm	0.02 ppm	0.00
	42.74 ppm	10	42.69 ppm	0.02 ppm	-0.12

[a] Based on NBS's letter notifying EPA that the batch has met CRM specifications.

[b] $\text{Agreement} = 100 \left[\frac{\text{Audit Value} - \text{Producer's Value}}{\text{Producer's Value}} \right]$

Table 13. Comparison of Producer's Measured Value with Audit Results for All Nitric Oxide in Nitrogen Batches

Nominal CRM Concentration	Producer's Measured Value[a]	Audit Results			Agreement (Percent Relative)[b]
		# of Values	Mean Measured Value	Standard Deviation	
100 ppm	93.2 ppm	10	93.70 ppm	0.18 ppm	+0.54
	93.2 ppm	10	93.43 ppm	0.13 ppm	+0.25
250 ppm	243.3 ppm	10	243.3 ppm	0.1 ppm	0.00
	243.7 ppm	10	243.3 ppm	0.2 ppm	-0.16
	236.4 ppm	10	236.4 ppm	0.1 ppm	0.00
	236.4 ppm	10	235.9 ppm	0.2 ppm	-0.21
500 ppm	470. ppm	10	470.3 ppm	0.3 ppm	+0.06
	471. ppm	10	470.2 ppm	0.4 ppm	-0.17
1000 ppm	953.4 ppm[c]	12	957.2 ppm	1.0 ppm	+0.40
	955.1 ppm[c]	10	958.6 ppm	0.9 ppm	+0.37

[a] Based on NBS's letter notifying EPA that the batch has met CRM specifications.

[b] $\text{Agreement} = 100 \left[\frac{\text{Audit Value} - \text{Producer's Value}}{\text{Producer's Value}} \right]$

[c] This batch has not been certified because of stability problems. The producer's measured value is the mean of the first and second analyses.

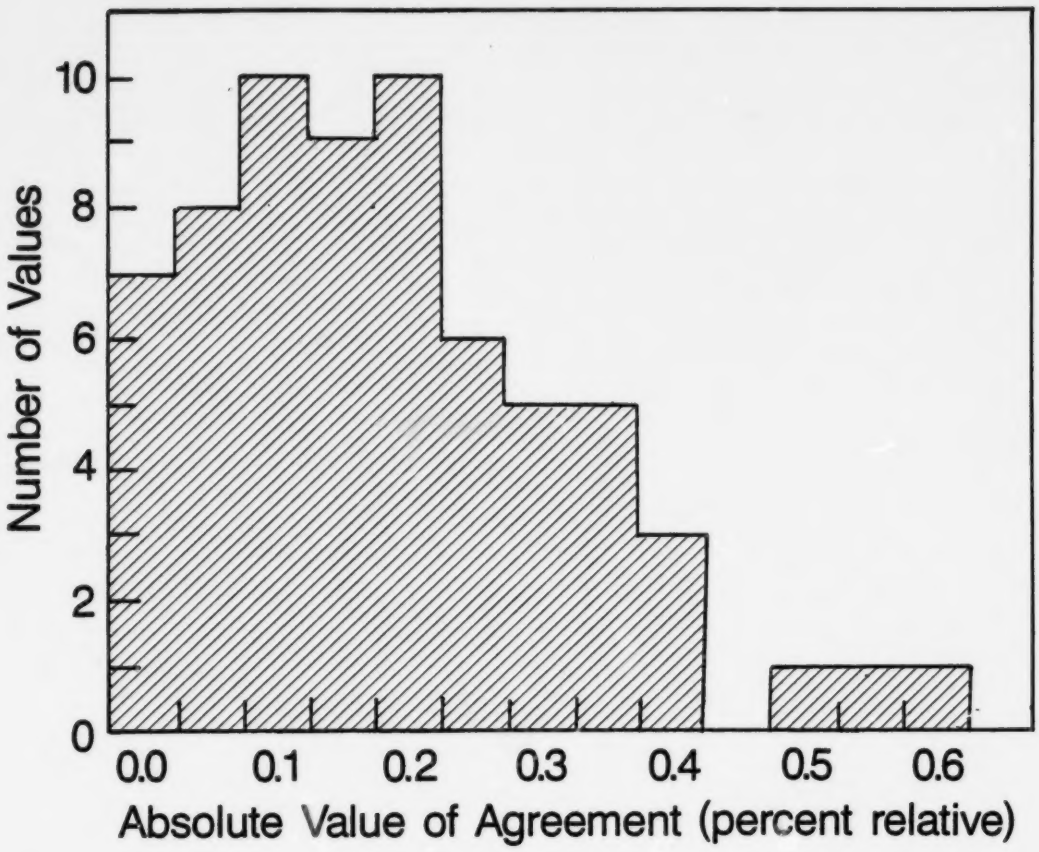

Figure 4. Frequency distribution for the agreement between producer and auditor analytical results for CRM batched

samples had a mean COV of 0.09 percent and a maximum COV of 0.19 percent. Although these COVs are within the limits specified by the NBS/EPA traceability document, the COVs for the high concentration carbon monoxide measurements need some improvement.

SECTION 6
CRM AVAILABILITY

A list of all CRM batches which have been approved for sale is given in Table 14. The inclusion of a batch in this list should not be construed to mean that this batch is still in stock or that this batch is within its certification period. The CRM producers should be consulted concerning the current or future availability of any particular CRM. The producers may be contacted at the following addresses and phone numbers.

Airco Industrial Gases
River and Union Landing Roads
Riverton, New Jersey 08077
(609) 829-7878

Air Products and Chemicals, Inc.
P. O. Box 351
Tamaqua, Pennsylvania 18252
(717) 467-2981

Matheson Gas Products
30 Seaview Drive
Secaucus, New Jersey 07094
(201) 867-4100

Scott Specialty Gases
Route 611
Plumsteadville, Pennsylvania 18949
(215) 766-8861

Table 14. List of CRM's Which Have Been Approved for Sale

CRM Composition	CRM Concentration	CRM Producer			
		Airco	Air Products	Matheson	Scott
Carbon Monoxide in Nitrogen	10 ppm			Yes	Yes
	25 ppm	Yes			Yes
	50 ppm	Yes	Yes	Yes	Yes
	100 ppm	Yes			
	250 ppm	Yes			Yes
	500 ppm	Yes	Yes		
	1000 ppm	Yes			Yes
	2500 ppm	Yes			Yes
	5000 ppm	Yes	Yes		Yes
	1%		Yes		
	2%		Yes		
	4%	Yes			
	8%	Yes	Yes		
Carbon Monoxide in Air	43 ppm	Yes			Yes
Nitric Oxide in Nitrogen	100 ppm	Yes			
	250 ppm	Yes			Yes
	500 ppm	Yes			

SECTION 7
CONCLUSIONS

This report has dealt with the performance audit program for CRMs. The producers' measured values were compared with the audit results for two audit samples from each of 33 batches. In general, the agreement between the values has been within 0.5 percent relative. This comparison demonstrates that specialty gas producers can prepare and analyze CRMs with an accuracy approaching that of SRMs. Additional data have been presented concerning the long-term stability of CRMs. Based on these data, it appears that CRMs are stable over their certification periods.

SECTION 8
ACKNOWLEDGEMENTS

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11. EPA maintains a current list of batches of CRMs that have been approved for sale and of their vendors. A copy of this list may be obtained by calling Ms. Katherine A. Powers at (919) 541-2198, or by writing her at the following address: Quality Assurance Division (MD-77), Environmental Monitoring Systems Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina 27711.

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